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THE ELECTRODEPOSITION OF LOW CONTRACTION CHROMIUM USING HIGH/LOW CURRENT PULSING

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TABLE OF CONTENTS

INTRODUCTION	1
EXPERIMENTAL PROCEDURE	1
RESULTS AND DISCUSSION	2
Effects of High/Low Current Pulsing	2
CONCLUSIONS	3
REFERENCES	4

List of Illustrations

1. A schematic diagram of the high/low current pulsing cell	5
2. The high/low current pulse profile for each of the three high/low current densities tested	6
3. The effects of high/low current pulse plating on the (a) CCE, (b) hardness, and (c) UTS of LC chromium electrodeposits	7
4. SEM topographical photomicrographs of LC chromium electrodeposited using high/low current pulse plating	8
5. SEM photomicrographs of the cross-sectional microstructure of LC chromium using high/low current pulse plating	9
6. XRD patterns of LC chromium electrodeposited using high/low current pulsing	10

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INTRODUCTION

Conventional unipolar (on/off) pulse plating, which is the use of interrupted direct current (dc), can improve the microstructure and mechanical properties of electrodeposited chromium when certain pulsing frequencies, duty cycles, and plating conditions are used (refs 1-5). The pulses, often employed at a rate of 10 to 10,000 times per second, affect the way the metal ions deposit to the substrate. During conventional dc plating, the rate at which the metal ions deposit is greater than the diffusion rate of the ions, resulting in a concentration gradient in the immediate area of the cathode (ref 6). In addition, an electric field in the electrolyte characterizes itself into a direction that influences and produces polarization near the edges of the cathode resulting in a thicker deposit near the end of the cathode (ref 7). When conventional pulse current is used instead of direct current, the current is on for a short time interval sufficient to deposit all metal ions in the immediate vicinity of the cathode. During the off-time of the pulse cycle, solution equilibrium is re-established, eliminating any concentration gradient that would exist. In addition, the resulting level of polarization on the surface of the cathode, across the layer of diffusion, is evenly distributed. Faust, Schaer and Semones (ref 8) have reported that during the off-time of pulse plating, the unstable chromium hydride layer, formed during chromium deposition, decomposes before the next on-time is applied. The chromium hydride layer has been linked to internal cracks and high residual stresses within the chromium. Therefore, the pulsing of chromium offers the advantages of reducing the amount of chromium hydride present.

The concept of high/low current pulse (HLCP) is similar to on/off pulse plating, except that there is no "off period" during plating. There is a high current period equivalent to the on-time in normal pulse plating. In addition, there is a low current period that has similar characteristics of the off-time in conventional pulse plating. If the current is at a low enough value, the metal ions will diffuse faster than their deposition rate, and as a result, the ion concentration in the immediate vicinity of the cathode will not be depleted. In theory, the advantage of the HLCP over the on/off current pulse is that you can continue to plate during the low current cycle without depleting the ions in the cathodic film. As a result, higher deposition rates may be obtained.

It also appears that HLCP may be more beneficial in terms of grain growth than on/off current pulsing. During the high current period, a large number of nuclei are generated (as with the on-time during on/off pulsing). However, unlike the off period in on/off pulsing, the grains continue to grow during the low current cycle. With each high current cycle, growth centers are generated, and with each low current cycle, the nuclei grow bigger and thicker. Eventually the growth centers coalesce and develop into larger, individual dome-like nodules. These large oriented dome-like nodules in the chromium deposits are often characteristic of good microstructure and mechanical properties.

This study systematically investigates the HLCP of low contraction (LC) chromium to determine which HLCP conditions, if any, improve the mechanical and microstructural properties of dc-plated LC chromium electrodeposits. The purpose of this study is to determine the optimal HLCP cycle by correlating the cycle with the microstructure, topography, ultimate tensile strength (UTS), preferred orientation and hardness of the chromium deposit, and the current cathode efficiency (CCE) of the plating process.

EXPERIMENTAL PROCEDURE

The experimental procedure was carried out exactly as described in previous reports (ref 5) except for the pulsing conditions. A conventional chromic acid bath was used consisting of a chromic acid/sulfuric acid ratio of 100/1, a trivalent chromium concentration of 4.0 g/l, and a bath temperature of 85°C. A schematic diagram showing the high/low pulse plating cell is shown in Figure 1.

The HLCP was conducted at three high/low current density ratios: 200/100, 200/60, and 200/30 A/dm². For each high/low current density ratio tested, the low current density (LCD) time was kept constant at 30 ms, and the high current density (HCD) time was varied from 0.6 to 60 ms (see Figure 2).

RESULTS AND DISCUSSION

Four specimens were prepared for each of the plating conditions investigated. The CCE, microhardness, and UTS results are the average of measurements for the four specimens.

Effects of High/Low Current Pulsing

The effects of HLCP on the mechanical properties of LC chromium are shown in Figure 3. Figure 3a shows that for each of the three pulse current density ratios tested, the CCE increased as the HCD time was increased. This increase was much more pronounced at 200/60 and 200/30 A/dm² with the CCE increasing from 5 to 22 percent. The 200/100 A/dm² HLCP resulted in significantly higher CCEs, especially for HCD times in the 0.6 to 30-ms regime. These findings are consistent with chromium electrodeposition; higher current densities usually result in higher CCEs. All of the 200/100 A/dm² conditions resulted in CCEs over 21 percent--a significant improvement over the 11 percent CCE obtained when dc plating LC chromium (ref 9).

The effects of each HLCP condition on the microhardness of the deposits are shown in Figure 3b. In general, the hardness tended to decrease as the HCD time increased. This is a result of grain growth initiation during the HCD (held constant at 200 A/dm²). Grains are initiated during the HCD and continue to grow upward during the LCD. If the HCD time is for a short enough interval, the base of the grain will be small and the full grain will have a rectangular shape. When these rectangular grains coalesce, they leave few voids, and the hardness tends to be higher. However, if the HCD time is long, the base of the grain will be large, and the full grain will be pyramidal in shape. When these pyramidal grains coalesce, they leave many voids, and as a result, the hardness tends to be smaller. When the HCD time was 0.6 ms, all three current density ratios tested yielded hardness greater than 760 KHN, the optimal hardness obtained when dc plating LC chromium (ref 9).

The effects of each HLCP condition on the UTS of the deposit are shown in Figure 3c. As with the hardness, the UTS values tended to decrease as the HCD times increased. In addition, the 200/100 A/dm² current density ratio again resulted in the highest UTS regardless of the HCD time. The maximum UTS obtained, 25.8 Ksi at 200/100 A/dm² for 0.6/30 ms, was still significantly lower than the optimal 87 Ksi obtained while dc plating LC chromium (ref 9).

When the HCD time was greater than 30 ms, tensile specimens broke prematurely for all three current density ratios studied. As a result, there are no UTS values shown in Figure 3c for HCD times greater than 30 ms. This premature failure can best be understood when the topography and cross-sectional microstructure at each of the conditions tested is observed. Figure 4 shows the scanning electron microscope (SEM) topographical photomicrographs for each of the conditions tested. A flake-like grain structure resembling a pattern of interwoven platelet was observed when the HCD time was 30 ms or greater and the LCD was 60 A/dm² or less. These structures explain why the tensile strengths were so low at these conditions. Only when the HCD time was less than 3.0 ms and the LCD was greater than 30 A/dm², did the topography represent a hemispherical nodular appearance typical of dc-plated LC chromium.

The SEM cross-sectional photomicrographs for each HLCP (shown in Figure 5) also support the low UTS values shown in Figure 3c. Microcracks can be observed in the cross section when the HCD time was 10 ms or greater and the LCD was 60 A/dm² or less. These were the only conditions that did not yield a typical fibrous grain microstructure associated with LC chromium.

A series of x-ray diffraction (XRD) patterns for each HLCP condition studied is shown in Figure 6. Most of the patterns for the 200/60 and 200/30 A/dm² pulse series show several peaks with the relative intensity of the <110> peak being highest. This is characteristic of a chromium powder pattern with no major preferred orientation. However, the 200/100 A/dm² current density ratio shows a distinct <211> preferred orientation with the relative intensity of the <211> peak highest for all six HCD times tested. This may account for the higher tensile strengths seen in Figure 3c for the 200/100 A/dm² current density ratio. LC chromium electrodeposited by direct current also has a <211> preferred orientation.

CONCLUSIONS

The electrodeposition of LC chromium by high/low current pulsing at current density ratios of 200/100, 200/60, and 200/30 A/dm² was evaluated and compared to dc-plated LC chromium. Based on the results of experimental studies, the following conclusions can be made:

1. Electrodepositing LC chromium using an HLCP condition of 200/100 A/dm² with an HCD time between 0.6 and 10 ms and an LCD of 30 ms results in improvements to the CCE and microhardness of the deposit as compared to values obtained in dc plating.
2. Hardness values in excess of 900 KHN can be obtained when the HLCP condition is the following: 200/100 A/dm² with an HCD time between 0.6 and 10 ms and an LCD time of 30 ms. This is a 12 percent increase in the optimal hardness obtained through dc plating of LC chromium.
3. CCEs in excess of 22.1 percent can be obtained when the above HLCP conditions are used. This is a 91 percent increase over the optimal CCE obtained through dc plating.
4. The maximum UTS values obtained by HLCP, 25.8 Ksi, are still 67 percent lower than those obtained through dc plating. HLCP does not appear to reduce the microstresses in the chromium deposits.
5. Electrodeposits produced at an HLCP condition of 200/100 A/dm² with HCD times between 0.6 and 10 ms and an LCD time of 30 ms are crack-free with a typical columnar microstructure of fine cross fibrous grains and a <211> preferred orientation.

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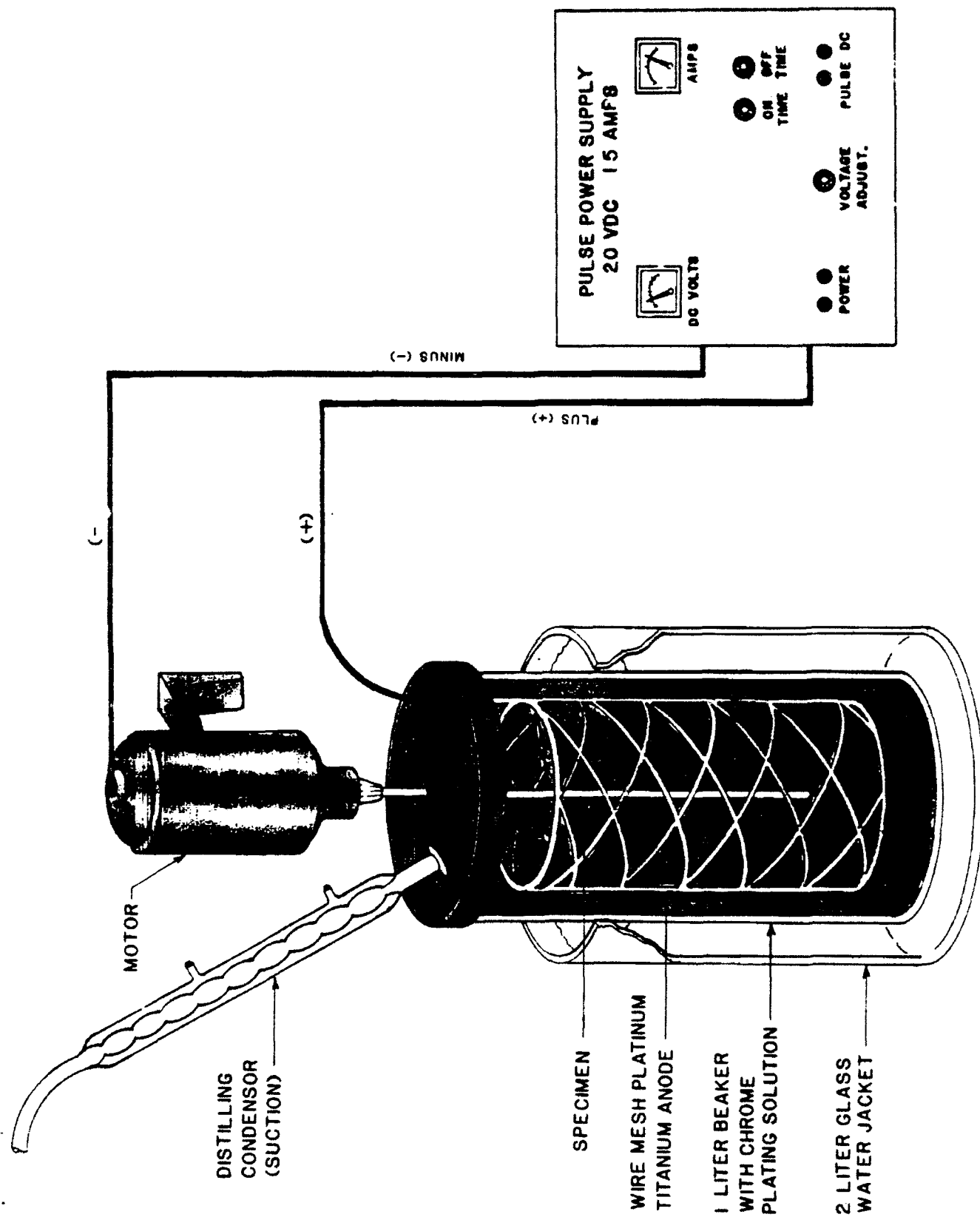


Figure 1. A schematic diagram of the high/low current pulsing cell.

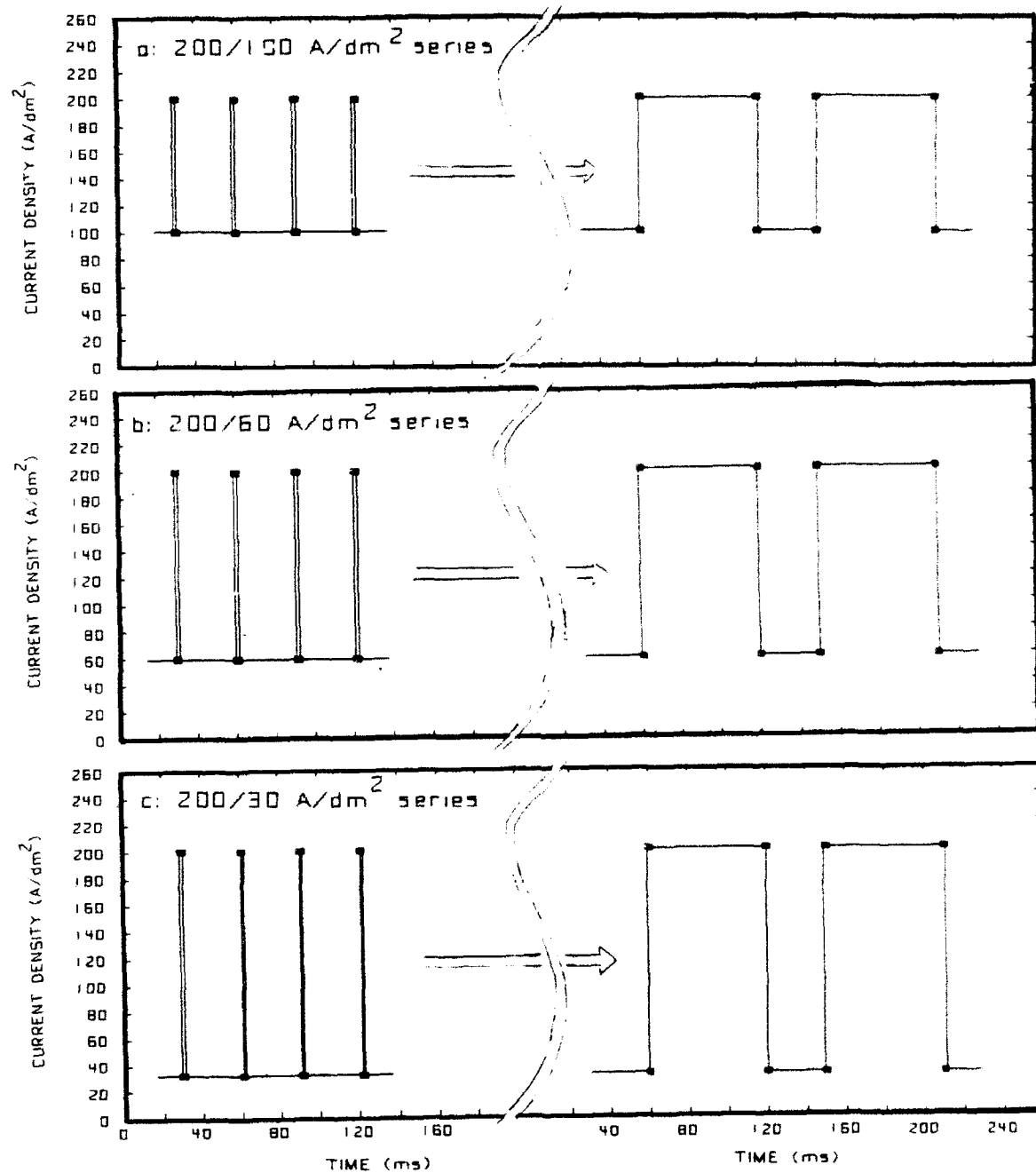


Figure 2. The high/low current pulse profile for each of the three high/low current densities tested.

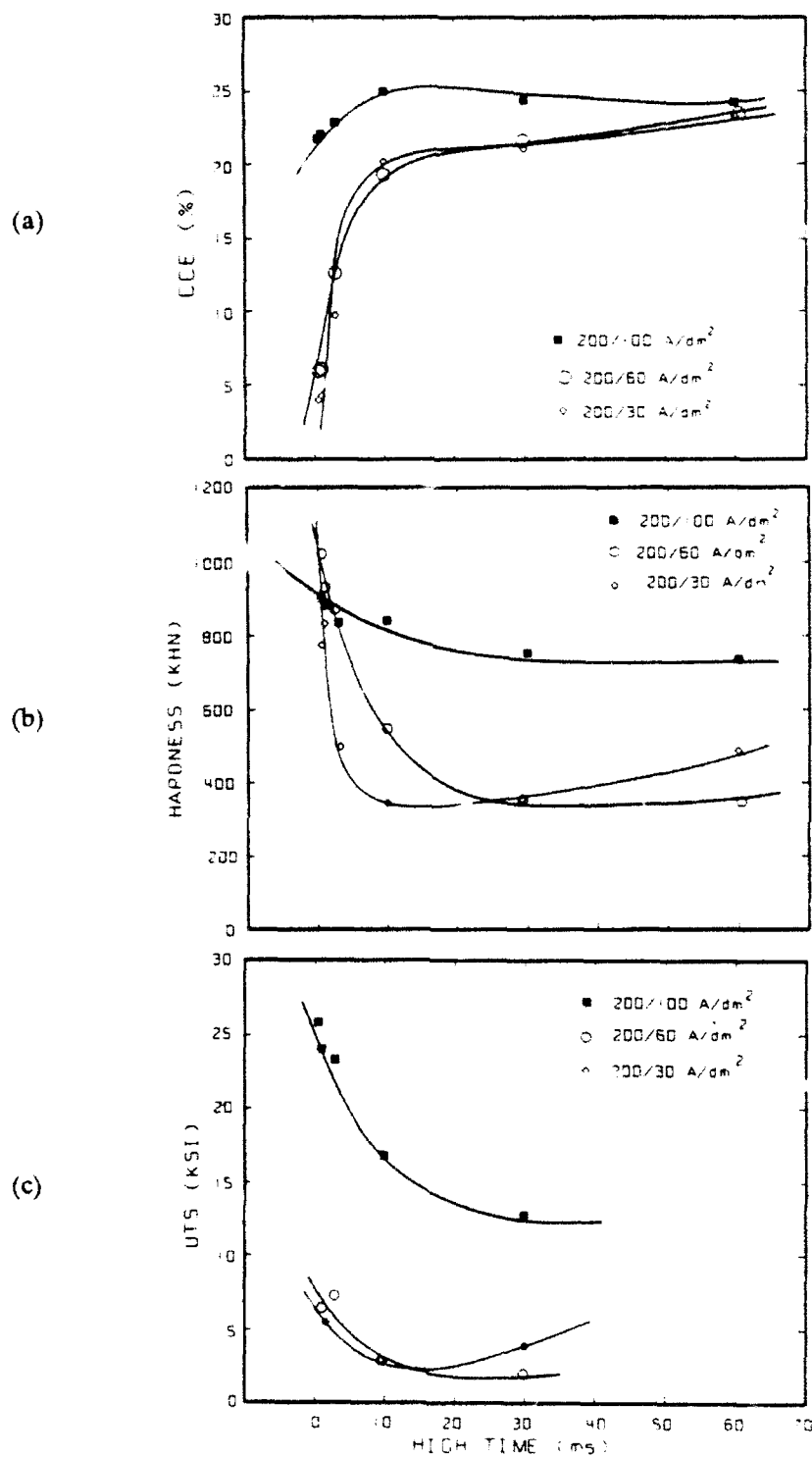


Figure 3. The effects of high/low current pulse plating on the (a) CCE, (b) hardness, and (c) UTS of LC chromium electrodeposits. The low current density time was kept constant at 30 ms.

HIGH TIME (ms)

0.6
1.0
3.0
10.0
30.0
60.0

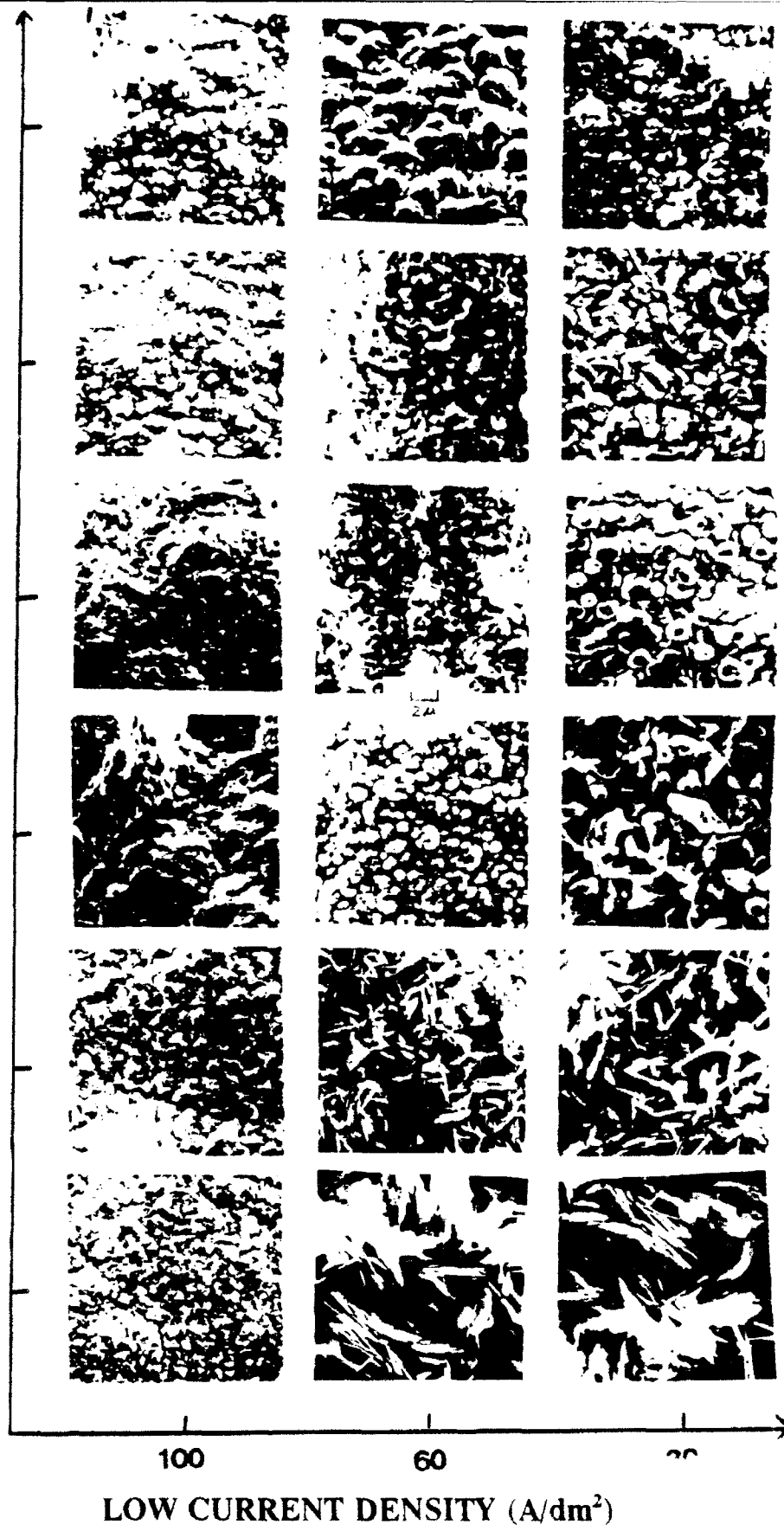


Figure 4. SEM topographical photomicrographs of LC chromium electrodeposited using high/low current pulse plating. The high current density was kept constant at 200/dm² and the low time was kept constant at 30 ms.

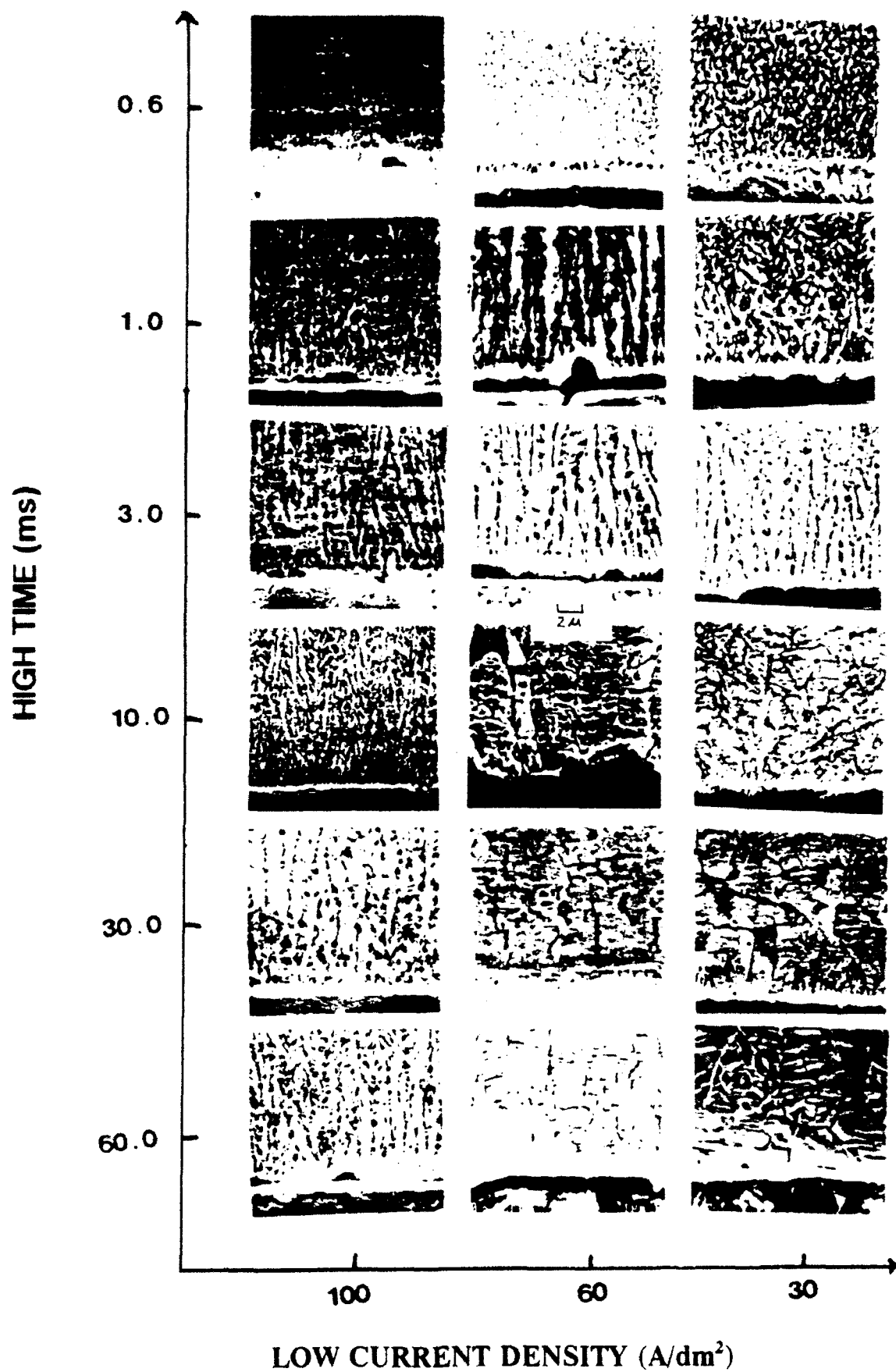


Figure 5. SEM photomicrographs of the cross-sectional microstructure of LC chromium using high/low current pulse plating. The high current density was kept constant at 200 A/dm² and the low time was kept constant at 30 ms.

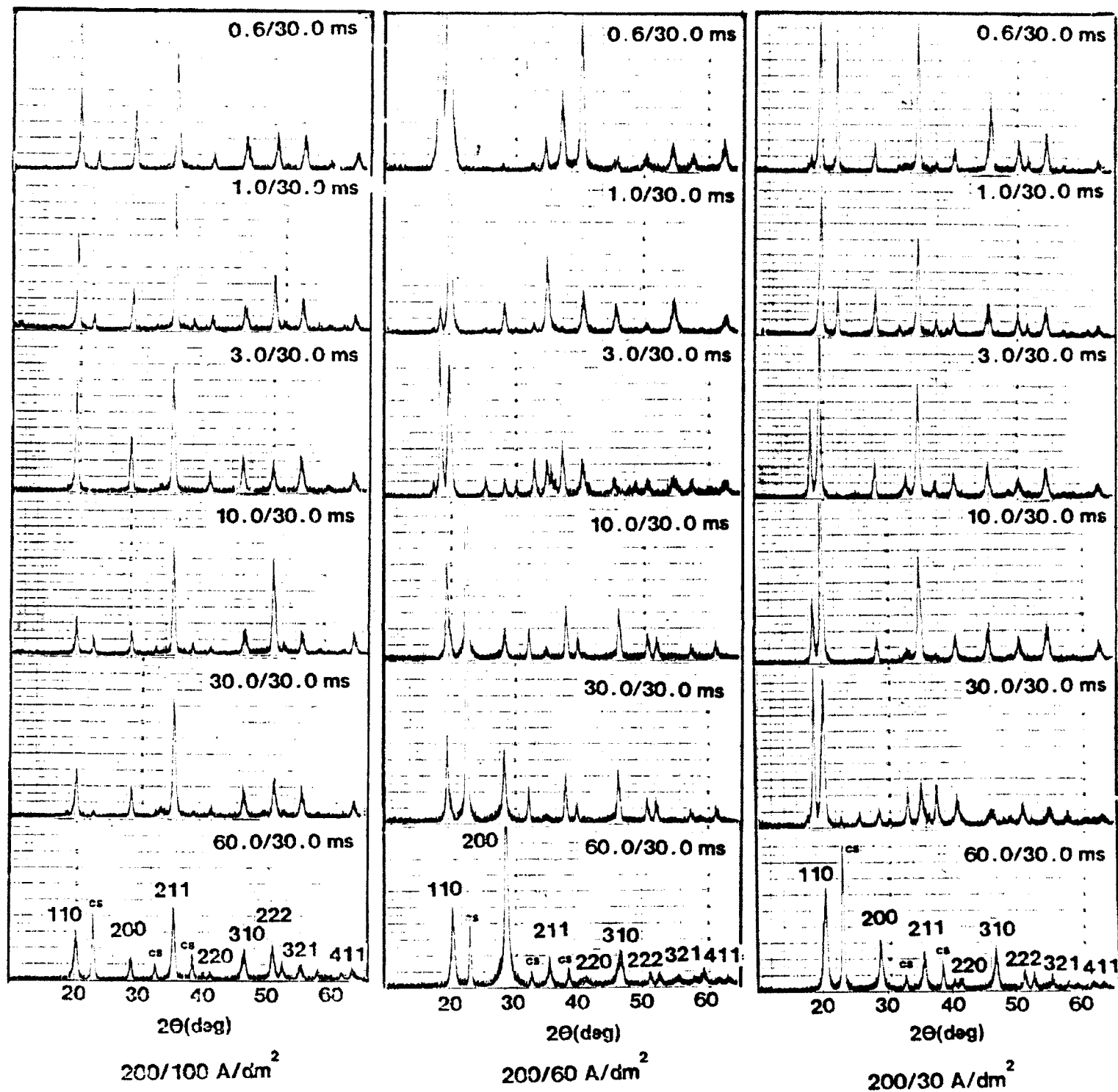


Figure 6. XRD patterns of LC chromium electrodeposited using high/low current pulsing.

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